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Electronic supplementary information

Reversible Organohydrogels Based on Dynamic Hydrogen Bonding among Water, Dimethyl Sulfoxide, and Polyethylene Glycol

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Materials

Dimethyl sulfoxide (DMSO, 99.9%) was purchased from Macklin. Polyethylene glycol (PEG, hydroxyl-terminated, CAS: 25322-68-3) with an M_w of 400, 2,000, 4,000, 5,000, 6,000, 8,000, 10,000, and 20,000 was purchased from Sigma-Aldrich. Ultra-pure water (18.2 MΩ·cm) was used to prepare organohydrogels.

Preparation of organohydrogels by the one-step method

There are three ways to prepare organohydrogels in one step: PEG was dissolved in water to make the aqueous solution, which further would be mixed with DMSO; PEG was dissolved in DMSO to make the organic solution, which further would be mixed with water; DMSO and water were mixed and heated to 70°C in prior to adding PEG, then the PEG binary solution was cooled to form organohydrogels. PEG with an M_w of 20,000 was used to prepare organohydrogels for characterizations.

Calculation by first-principles density functional (DFT) theory

The adsorption energy calculations of H_2O in PEG-H_2O-PEG, PEG-H_2O-DMSO, PEG-H_2O-H_2O, DMSO-H_2O-DMSO, DMSO-H_2O-H_2O, and H_2O-DMSO-H_2O were theoretically performed by the Gaussian 16 suite of programs [1]. The media was composed of 30 vol.% water and 70 vol.% DMSO. The geometry optimization was carried out by the B3LYP-D3BJ/TZVP level of theory. The vibrational frequencies of the optimized structures were calculated simultaneously and equivalently. The local energy minimum on the potential energy surface was used to indicate the structures by confirming the real vibrational frequencies. The solvent effect was included in the calculations based on the Polarizable Continuum Model (PCM) using the integral equation formalism variant (IEFPCM). The single point energies were calculated at the B3LYP-D3BJ/ma-TZVPP level of theory. The Atoms in Molecules (AIM) analysis was performed by using the Multiwfn software to estimate the inter-molecular hydrogen bonding energies in different sites based on the electron density distribution at the bond critical points (BCP) [2-4].

Fourier transform infrared (FTIR) spectroscopy

The data of FTIR was measured by the Fourier infrared spectrometer (Nicolet, iS50) equipped with a temperature control module. All liquids and organogels were tested by the attenuated total reflection (ATR) accessory, while solids were tested by the transmission mode. The wavenumber range was from 600 to 4000 cm^{-1}, the ambient temperature of testing unheated samples was set as 20°C, and all data were normalized as appropriate.

Micro-CT imaging of organohydrogels

Micro-CT images were carried out by the high-resolution micro-CT scanner (Bruker, SKYSCAN1272). The scan scope was acquired over 1000·1000 μm, and the resolution was set as 500 nm. The calculation of fractal dimension was conducted using Image J software. Images were first binarized and segmented, and then the Fractal Box Count plugin was used to calculate the fractal dimension.

Differential scanning calorimetry (DSC)

Thermal analyses were conducted by differential scanning calorimeter (METTLER TOLEDO, DSC1). The binary systems with 1, 5, 10, 15, 20, 25, 30, 35, 40, and 99 vol.% water were measured from 60 to 0°C and 0 to 60°C, respectively. The change rate of temperature was 2 °C/min. The soaking time before cooling and heating was 10 min. The low-temperature testing of the organohydrogel was cycled once between 0 and –70°C at a rate of 2 °C/min. The calculation of the relative crystallinity of PEG in organohydrogels was conducted following the equation:

$$Relative\ crystallinity\ (\%) = \frac{M_{OHG} \times \Delta H_{OHG}}{M_{PEG} \times \Delta H_{PEG}} \times 100$$

where M_{OHG} and M_{PEG} are the mass of organohydrogels and PEG in organohydrogels, and ΔH_{OHG} and ΔH_{PEG} are the enthalpies of organohydrogels and neat PEG during cooling.

Rheological measurement

The rheology of organohydrogels was investigated by the rotational rheometer (Anton Paar, MCR302). Strain sweep was performed from 0.001 to 100% (1 Hz), temperature sweep was cycled once between 5 and 55°C (0.01% strain and 1 Hz), and cooling sweep started at 10°C and ended at –25°C (0.01% strain and 1 Hz). The thixotropic ring was obtained from the cycled shear rate sweep between 0 and 130 s^{-1}.

Characterization of wide-angle scattering (WAXS) and X-ray diffraction (XRD)

WAXS and XRD measurements were performed by X-ray scatterer (Xenocs, Nano-inXider) and an X-ray diffractometer (Bruker, D8 ADVANCE), respectively. The testing q value was from 0.35 to 4 Å for WAXS. 2θ was from 5 to 60° for XRD measurement at 25°C.

Scanning electron (SEM), transmission electron (TEM), and polarized light microscopy

SEM and TEM images were observed by the cold field scanning electron microscope (HITACHI, SU-8010) and transmission electron microscope (HITACHI, H-7650), respectively. Polarized light micrographs were captured by the light microscope with the polarized light sheet (Nikon, E600POL). Organohydrogels were dried in ambient air before being observed by SEM. The organohydrogel would be diluted and filtered using the 0.8 μm filter membrane for the TEM measurement.

Drying resistance ability

The drying resistance ability of organohydrogels was measured at ambient air (indoor, Hangzhou, China) and dry condition (30% relative humidity and 20°C), respectively. The weight of organohydrogels was recorded for 1 week in ambient air, while that was recorded for 1 d in the dry condition.

Table S1. The adsorption energy of water connecting with PEG, DMSO, or water at two ends.

Adsorption energy (water, kcal/mol)		B side		
		PEG	DMSO	Water
A side	PEG	–12.133	–12.368	–11.982
	DMSO		–14.272	–13.106

Table S2. The DSC data of organohydrogels and the relative crystallinity of PEG in organohydrogels.

Water (vol.%)	Cooling				Heating				Relative crystallinity (%)
	T_{onset} (°C)	T_{peak} (°C)	T_{endset} (°C)	Exothermic enthalpy (J/g, Abs)	T_{onset} (°C)	T_{peak} (°C)	T_{endset} (°C)	Endothermic enthalpy (J/g, Abs)	
5	15.49 ± 0.12^{h}	11.71 ± 0.15^{h}	9.47 ± 0.10^{f}	4.45 ± 0.02^{g}	32.35 ± 0.13^{g}	35.66 ± 0.16^{h}	37.56 ± 0.13^{i}	4.95 ± 0.03^{f}	59.41 ± 0.27^{f}
10	24.27 ± 0.08^{f}	21.03 ± 0.13^{f}	14.34 ± 0.11^{e}	4.49 ± 0.01^{f}	34.41 ± 0.12^{f}	37.04 ± 0.14^{g}	38.80 ± 0.09^{h}	4.93 ± 0.01^{f}	59.94 ± 0.13^{f}
15	27.60 ± 0.11^{d}	24.81 ± 0.11^{d}	21.51 ± 0.10^{c}	4.82 ± 0.03^{e}	39.24 ± 0.08^{d}	41.36 ± 0.11^{e}	42.90 ± 0.14^{f}	4.97 ± 0.04^{f}	64.35 ± 0.40^{e}
20	32.00 ± 0.09^{b}	29.33 ± 0.09^{b}	27.06 ± 0.08^{a}	5.00 ± 0.02^{d}	41.71 ± 0.17^{c}	43.48 ± 0.09^{d}	45.08 ± 0.07^{d}	5.30 ± 0.02^{d}	66.75 ± 0.27^{d}
25	33.00 ± 0.05^{a}	29.90 ± 0.08^{a}	27.10 ± 0.12^{a}	5.96 ± 0.03^{a}	42.76 ± 0.11^{a}	45.23 ± 0.06^{a}	46.68 ± 0.12^{a}	6.19 ± 0.05^{a}	79.57 ± 0.40^{a}
30	31.51 ± 0.10^{c}	28.01 ± 0.12^{c}	25.06 ± 0.14^{b}	5.58 ± 0.03^{b}	42.89 ± 0.06^{a}	44.47 ± 0.12^{b}	46.29 ± 0.08^{b}	5.96 ± 0.02^{b}	74.50 ± 0.44^{b}
35	26.58 ± 0.12^{e}	22.81 ± 0.14^{e}	19.07 ± 0.16^{d}	5.21 ± 0.04^{c}	42.09 ± 0.09^{b}	43.92 ± 0.11^{c}	45.66 ± 0.09^{c}	5.58 ± 0.05^{c}	69.56 ± 0.53^{c}
40	20.75 ± 0.05^{g}	13.09 ± 0.17^{g}	0.63 ± 0.09^{g}	4.83 ± 0.02^{e}	39.09 ± 0.10^{d}	41.43 ± 0.08^{e}	43.13 ± 0.14^{e}	5.18 ± 0.01^{e}	64.48 ± 0.27^{e}
45	13.58 ± 0.07^{i}	8.52 ± 0.11^{i}	0.54 ± 0.06^{g}	2.94 ± 0.05^{h}	38.11 ± 0.12^{e}	39.20 ± 0.10^{f}	40.40 ± 0.12^{g}	3.03 ± 0.03^{g}	39.25 ± 0.67^{g}

Values are presented as means ± SD. a-i mean the significant difference ($p < 0.05$).

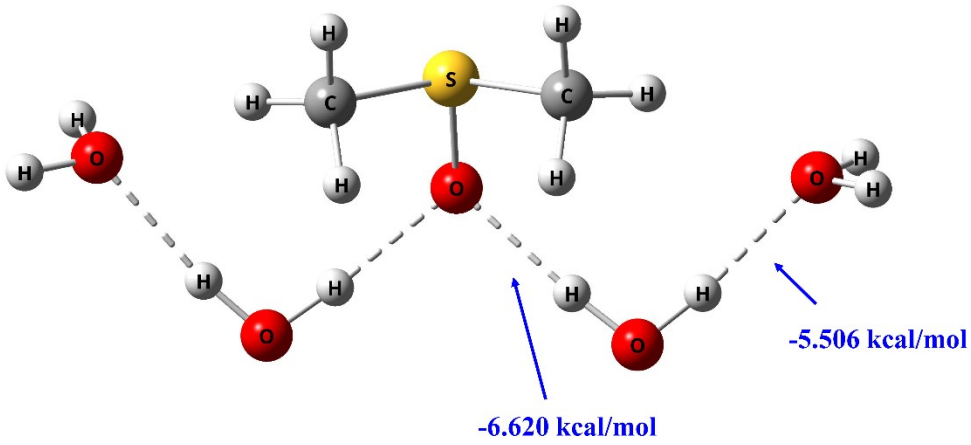

Figure S1. Optimized structure and DFT analysis of the water molecule connected with one H_2O and one DMSO (two H_2O bonded).

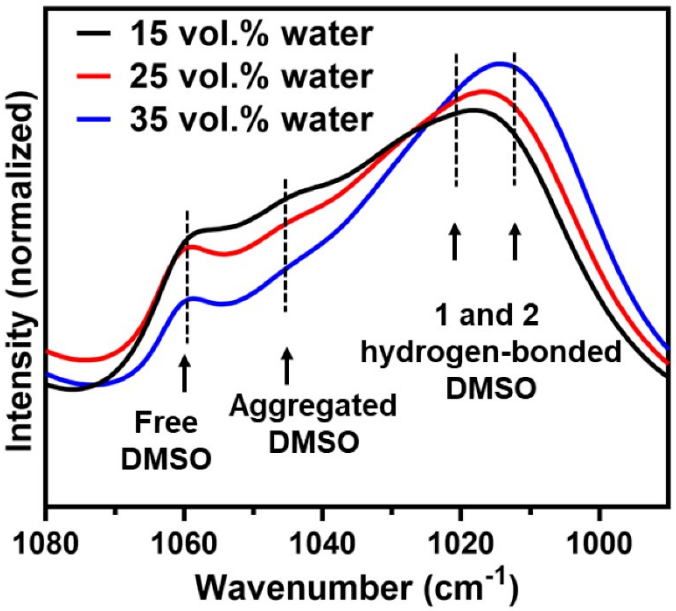

Figure S2. The FTIR data of organohydrogels (30 mg mL−1 of PEG) with 15, 25, and 35 vol% water, respectively.

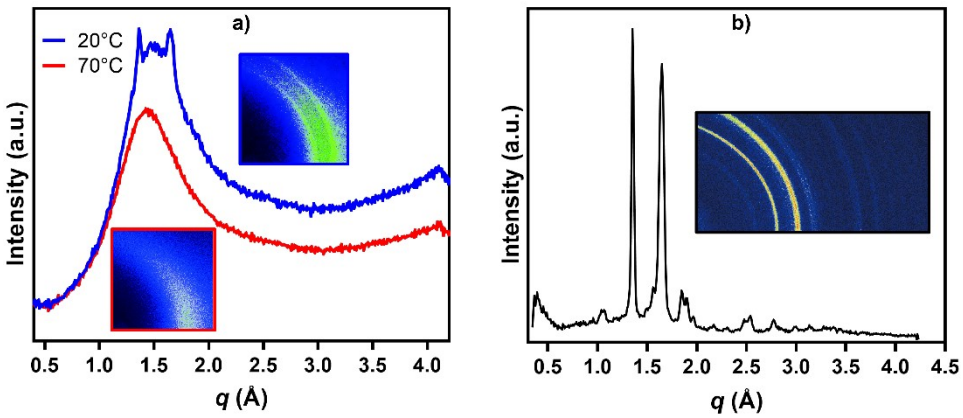

Figure S3. a) WAXS patterns of organohydrogels (30 mg/mL, 25 vol.% water) at 20°C (blue line) and 70°C (red line). b) WAXS pattern of neat PEG (Mw=20,000). Insets are corresponding 2D scattering patterns.

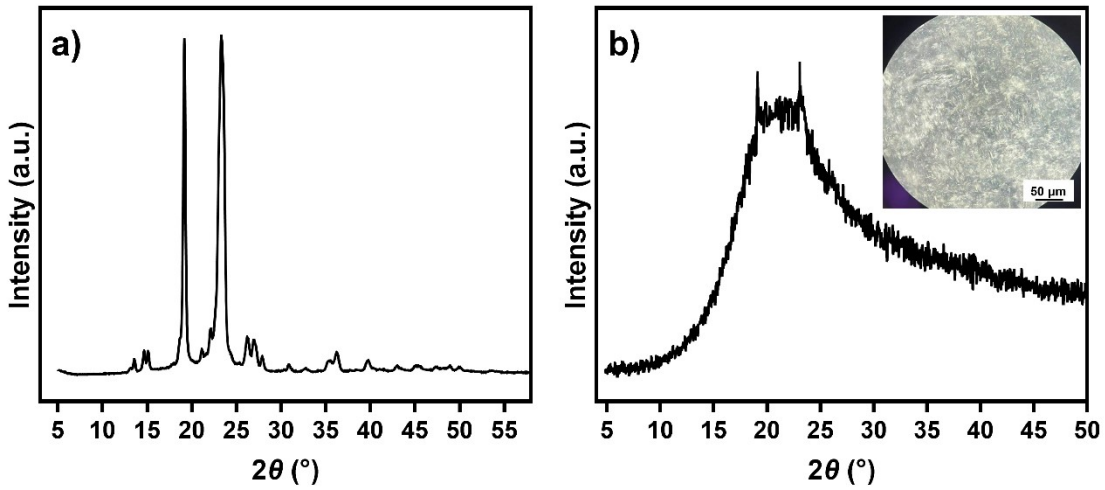

Figure S4. XRD data: a) neat PEG (Mw=20,000); b) the organohydrogel (30 mg/mL of PEG and 25 vol.% water), inset is the polarized-light micrograph of the organohydrogel.

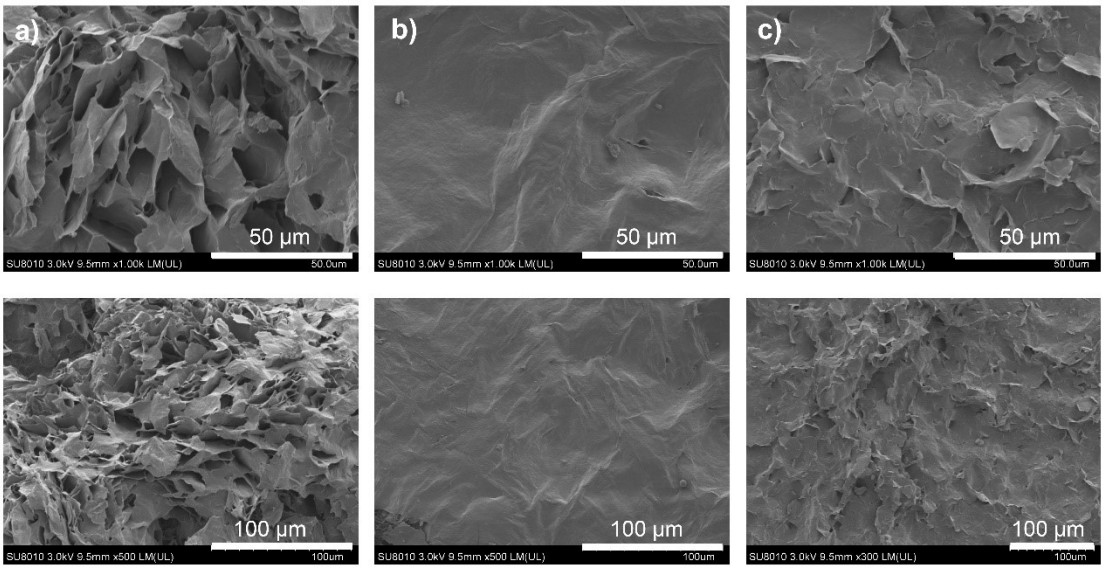

Figure S5. SEM micrographs of dried organohydrogels (30 mg/mL of PEG): a) the organohydrogel prepared by 30 vol.% water; b) the precipitation prepared by 10 vol.% water; the flocculation prepared by 10 vol.% water. The second row represents the corresponding enlarged micrographs.

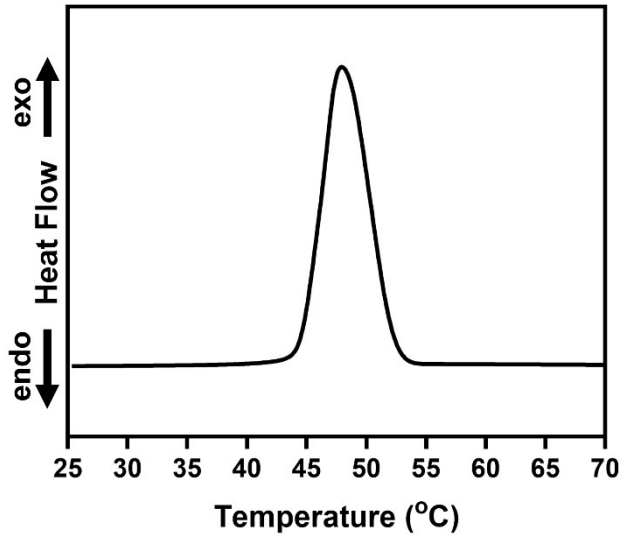

Figure S6. DSC data of cooling PEG (M_w=20,000) from 70 to 25°C. The exothermic enthalpy is 171.53 J/g, the peak temperature is 48.71°C, and the T_{onset} and T_{endset} are 52.39 and 44.93°C, respectively.

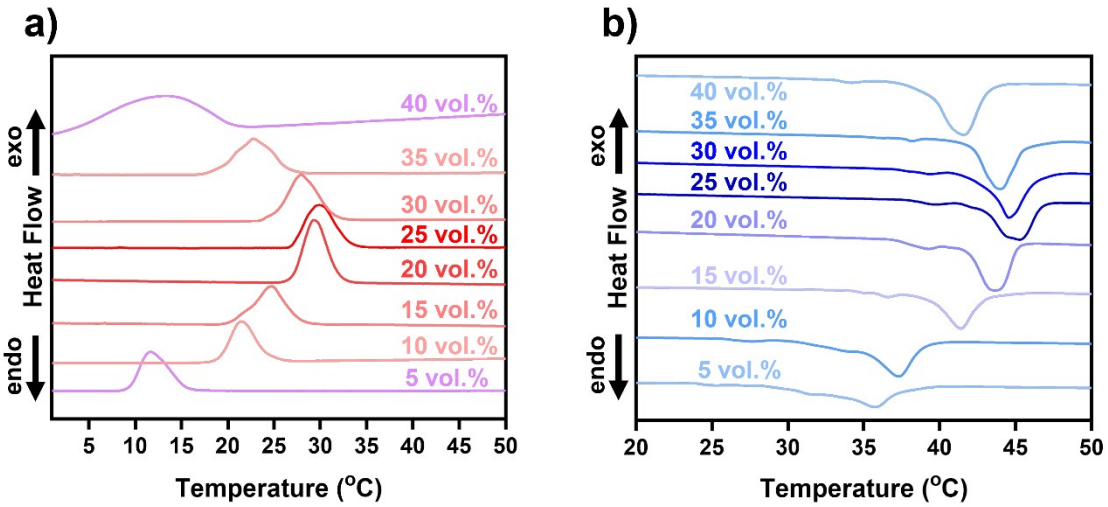

Figure S7. DSC data of organohydrogels (30 mg/mL of PEG) prepared by 5-40 vol.% water: a) the exothermic process of cooling; b) the endothermal process of heating. Detailed data can be found in Table S2.

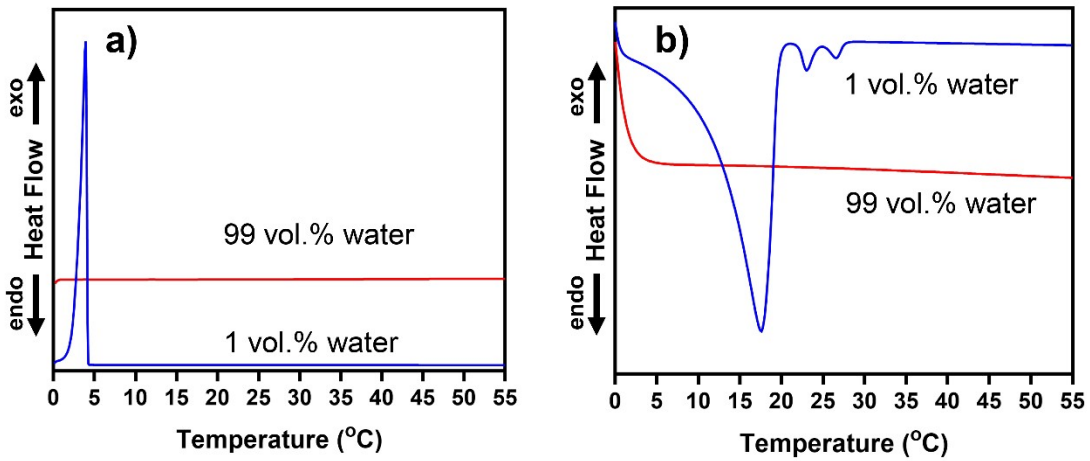

Figure S8. DSC data of the binary solutions with 99 and 1 vol.% water, respectively: a) DMSO in the group with 1 vol.% water is frozen at 4°C during the cooling process (118.24 J/g); b) the exothermal process during heating. No thermal fluctuations of PEG appear in the groups with 99 and 1 vol.% water.

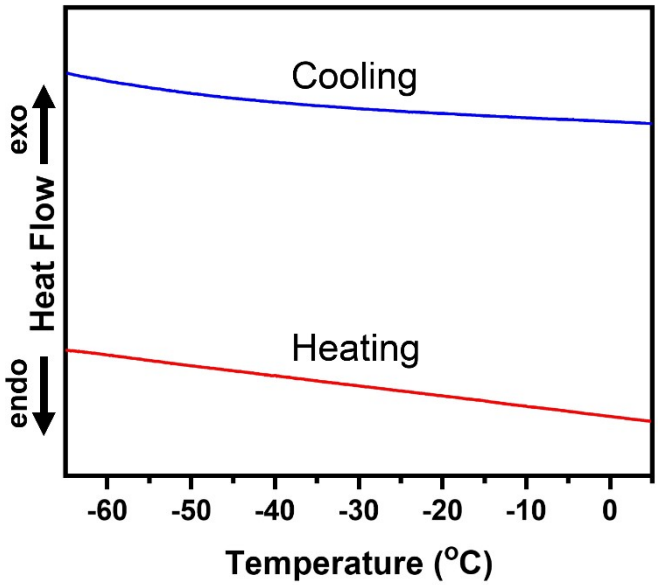

Figure S9. DSC data in the temperature range of –70 to 5°C of the organohydrogel (30 mg/mL of PEG) prepared by 25 vol.% water. No freezing of DMSO and water can be found.

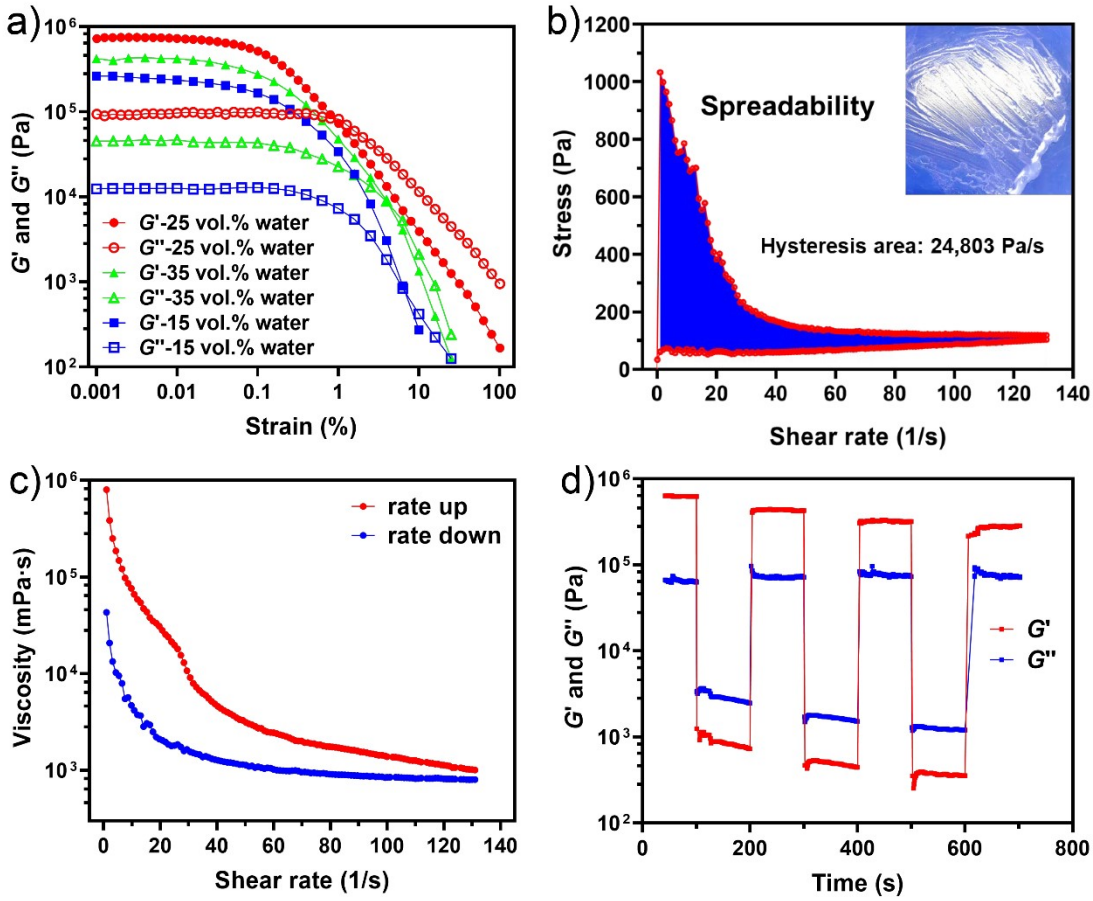

Figure S10. Rheological study of organohydrogels (30 mg/mL of PEG): a) strain sweep from 0.001 to 100% with the frequency of 1 Hz; b) and c) shear rate sweep between 0 to 130 s (25 vol.% water); d) time sweep with alternating 0.01 and 10% strain (1 Hz and 25 vol.% water).

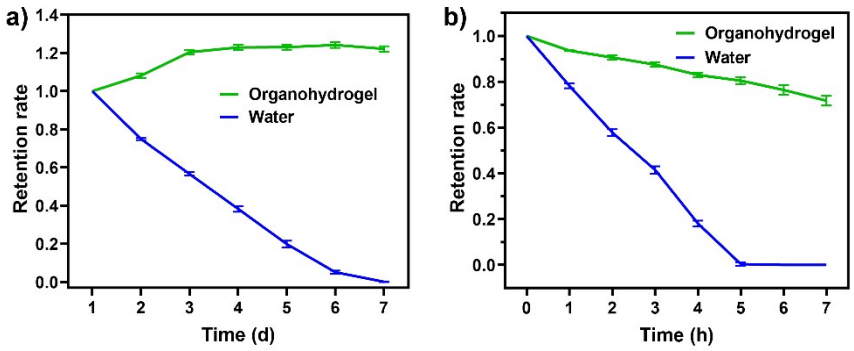

Figure S11. The moisture retention rate of organohydrogels in (a) ambient air for 7 d and (b) dried air (30% relative humidity) for 7 h, respectively.

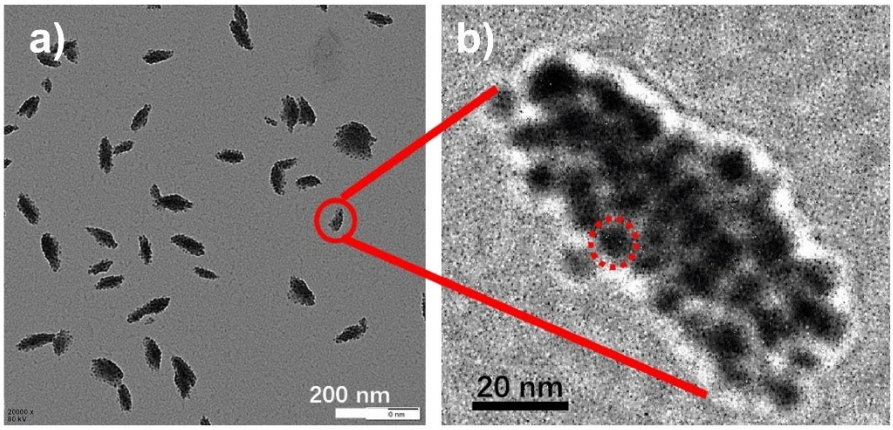

Figure S12. TEM micrographs of semicrystalline: a) the filtered crystal clusters (100-200 nm); b) the enlarged graph of a cluster composed of many crystal nuclei (10 nm).

References

1. M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, Williams, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman and D. J. Fox, *Journal*, 2016.
2. R. F. W. Bader, J. Halpen and M. L. H. Green, *Atoms in Molecules: A Quantum Theory*, Oxford

University Press, Oxford, 1990.
3. T. Lu and F. Chen, *J. Comput. Chem.*, 2012, **33**, 580-592.
4. S. Emamian, T. Lu, H. Kruse and H. Emamian, *J. Comput. Chem.*, 2019, **40**, 2868-2881.